M onthly
  E cumenical
    Letters from
    Laboratories
      Of
      N - M - R

      No. II

OTTAWA 2.

June 29, 1959.

Dr. Aksel A. Bothner-By,
Mellon Institute,
440 Fifth Avenue,
Pittsburgh 13, Penna.

Dear Aksel:

Enclosed please find the spectra of cis and trans butene oxide and propylene oxide. It is interesting to compare the CH_3-H spin coupling across the oxide ring and across the double bond (Mellonmr #4). In each case there seems to be a significant reduction in spin coupling when an oxygen is attached to the two carbon atoms. It can also be seen that the spin coupling for the trans isomer is less than for the cis isomer of the oxides but the reverse is probably true for the olefins. Unfortunately the resolution is not too good for the 60 Mc. spectra but following are the approximate results:

(a)

	J12 cycles/sec.	J13	J23	J24	J34
CH_3-C=C-H	6.6		18	8.7	

(b)

	J12 cycles/sec.	J13	J23	J24	J34
CH_3-C-C-H (oxide)	5.1	~0	2.4	9.6	5.3
CH_3-C≡C-CH_3	4.5				4.5

J12 cycles/sec.	J13	J23	J24	J34
4.5				4.5
4.5				4.5
4.3		~0		~0	4.3

(a) "High Resolution Nuclear Magnetic Resonance", J. A. Pople, W. G. Schneider, H. J. Bernstein, pg. 242.

(b) Mellonmr #8, pg. 4.

Following are a few comments on your monthly letters. I greatly appreciate the inclusion of the bibliography. Its thorough coverage of the foreign journals is especially commendable. The only question that arises is the suitability of including articles where a slight mention of proton resonance spectra is made in an article primarily devoted to synthesis or structure proof. This is really not a complaint but just a point for discussion.

I am very pleased to see that a compound symbol is being suggested for describing chemical shifts. I think it advisable that the reference compound be specifically stated in the symbol so that it will be applicable to other isotopes as well as protons. The suggestion to describe frequencies of individual lines ought to be useful in those cases where there is a complex spectrum, however, in most cases it is unnecessary to have the dual notation. This is a point in favor of the two methods of describing data since the more complex notation including ν's will only be needed in the more complex cases. My vote is for
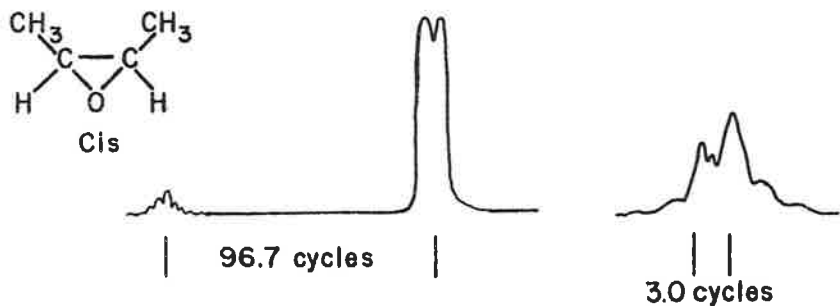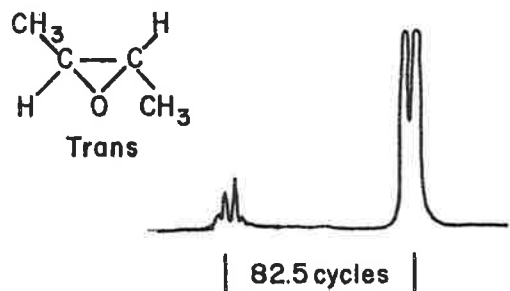
$$\delta \begin{matrix} \text{standard compound} \\ \text{int. or ext.} \end{matrix} , \text{ and } \nu^k_{i(j)}, \text{ only in those cases}$$

where calculations of chemical shift are not immediately obvious.

Yours truly,

S. Brownstein.

HIGHER RESOLUTION
60 Mc

|86.9 cycles|

|17.2 cycles|

Trans

|82.5 cycles|

Cis

|96.7 cycles|

3.0 cycles

DIVISION OF APPLIED CHEMISTRY

Cis

HIGHER RESOLUTION
40 Mc

X5

|71.5 cycles|

|5.6 cycles|

X5

|52.9 cycles|

|15.6 cycles|

DIVISION OF APPLIED CHEMISTRY

2.

RESEARCH DEPARTMENT
The Standard Oil Company (Ohio)
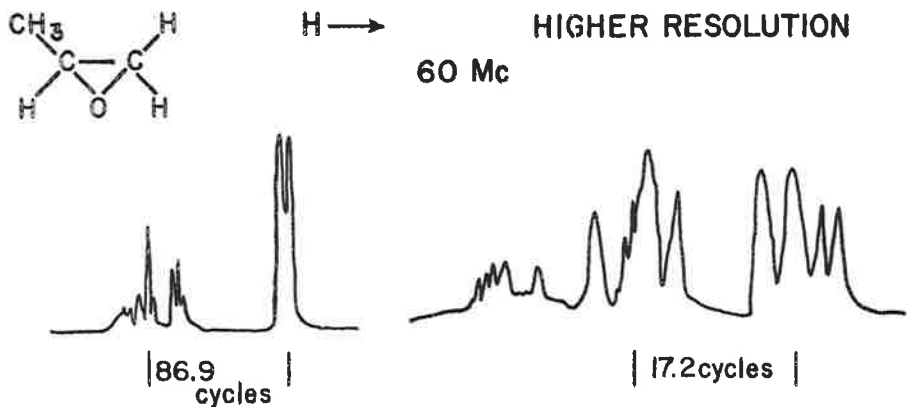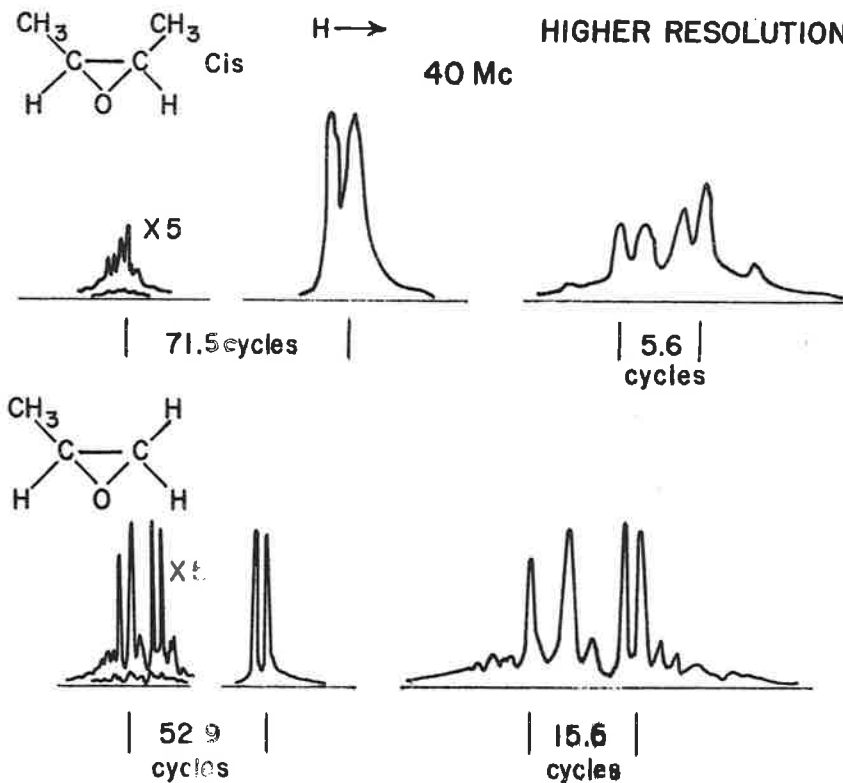
SOHIO MAGNET COOLING SYSTEM

W. R. Ritchey   May 13, 1959

In order to obtain high resolution NMR spectra, the cooling water to the magnet must be controlled. This applies not only to the temperature, but also to the flow rate. The sensitivity of the magnet to fluctuations in the water supply can be minimized by insulating the water pipes from the magnet yoke and adjusting the magnet coils so that they are not in contact with the pole pieces. The degree of control described below is more than adequate if the above two precautions are followed. This system (which can be built for less than $2,000) has been very satisfactory for the past several months, and thus far its short comings have not been realized.

Water is supplied to the magnet at the rate of 2.0 ± 1% gallons/minute, controlled to ± 0.1°F. The discharge from the magnet passes through a Ross heat exchanger during which its temperature is adjusted to be near final control temperature and is controlled to ± 1°F. The exchanger discharge then passes to the constant temperature bath in which the final regulation is performed.

The constant temperature bath is an Aminco type 4-8600, having a 16-gallon capacity and equipped with a 1000 watt heater and a refrigeration unit. It was modified in several respects: The 1/3 H.P. refrigeration unit was replaced with a 1/2 H.P. unit (1/3 H.P. would probably do the job, but ours was defective so we replaced it with a larger one). The bimetallic thermoregulator was replaced with a "Micro-Set Thermoregulator (Emil Griener #G-24653), having a sensitivity of ± 0.02°F., adjustable over the range of 50-220°F. The controller was redesigned in order to eliminate the 30 sec. time delay on both cycles so that we now have zero time delay on heating and 10 secs. on refrigerating (for protection of the refrigeration unit).

The water circulating pump is an Aurora DV-31, all bronze, turbine-type, pump-close coupled to 1/2 H.P. single-phase, 115-220 open type motor. The pump is very quiet. A series 30, Watts diaphragm pressure relief valve (model #SP-30) is adjusted to provide a constant flow of 2 gpm, utilizing a Brooks #FV-1110 Rotometer size #8, range 0.4 - 3.5 gpm. The flowmeter is equipped with a type AE alarm which is set so that any flow rate outside the 1.4 to 2.7 gpm range will shut off the power to the magnet. A pressure gage downstream from the flowmeter is also useful as an indication of the condition of the water filter on the magnet.

The heat exchanger is a 4-pass Ross type BCF Part #7M502A13, and the flow rate of city water is controlled with a Fulton Sylphon "Fultro Matic valve #1110C, range 55-105°F.

Thermometers are positioned on city water inlet and outlet, and magnet water outlet on the heat exchanger. Another is in the water bath and, finally, one downstream from the flowmeter.

If you desire more detail on the system, please contact the Research Department, The Standard Oil Company (Ohio), 4440 Warrensville Center Road, Cleveland 28, Ohio

# MAGNET COOLING SYSTEM
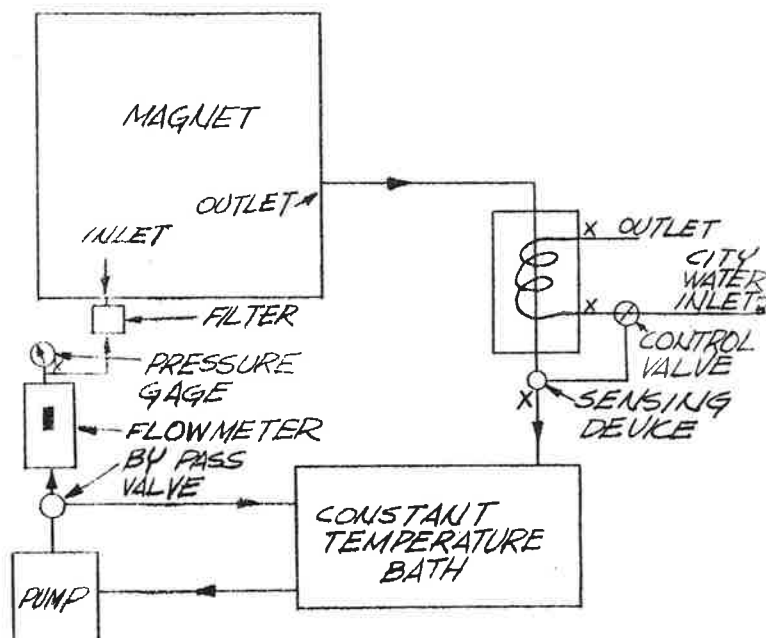
X DESIGNATES LOCATION OF THERMOMETER

Research Department
THE STANDARD OIL COMPANY (Ohio)
W. M. Ritchey - 4/30/59

RESEARCH DEPARTMENT
The Standard Oil Company (Ohio)

SOHIO TURBINE-PROBE INSERT ALIGNMENT TOOL

W. M. Ritchey   July 31, 1959

Erratic sample spinning has plagued us considerably in our hi-resolution studies. We found that correct turbine-probe insert alignment is as critical as constant air supply to the turbine. In order to accomplish correct alignment we constructed the alignment tool shown below.
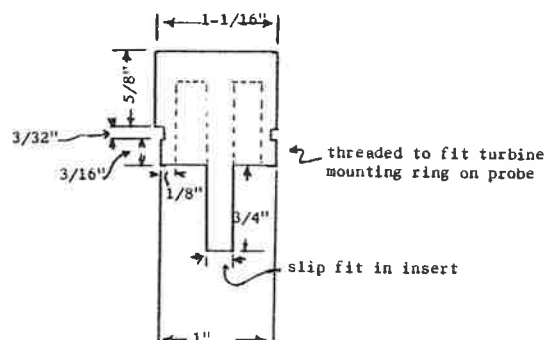
The alignment is accomplished by repositioning the turbine mounting ring until this device can screw-in and out freely. We found it necessary to enlarge the holes in the turbine mounting ring. Of course, any time the insert is removed from the probe, re-alignment is necessary. This has resulted in not only more consistent sweeps on the scope, but also in some resolution improvement in recorded spectra--all other factors being equal.

WMR:pmp
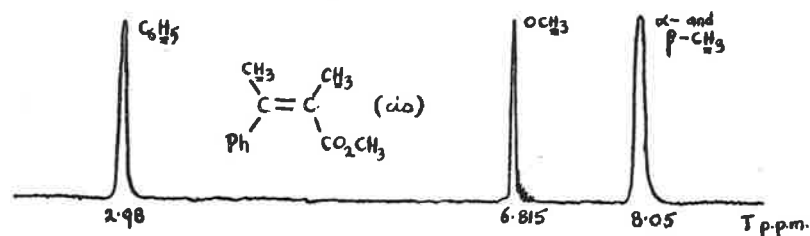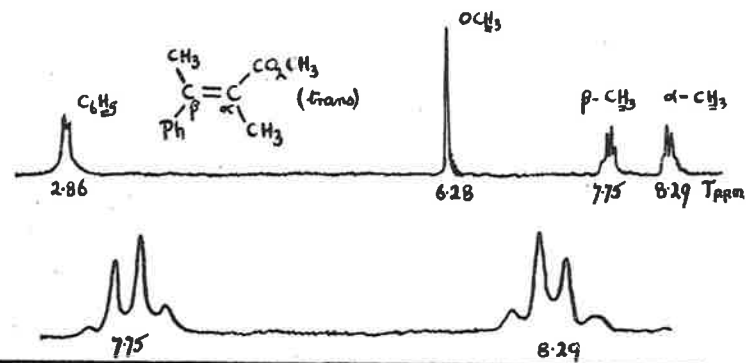
Spectra of the isomeric methyl $\alpha:\beta$-dimethylcinnamates (40 Mc/sec; 10% CCl_4 with T.M.S. as internal reference).

The observed line positions indicate that the aromatic nucleus is roughly perpendicular to the plane of the carbon-carbon double bond. Thus the methoxyl resonance in the cis ester is diamagnetically shifted by some 0.5 p.p.m indicating that this group lies over the top of the aromatic ring. In the trans ester the α-Me resonance suffers a similar diamagnetic shift for the same reason and at the same time the β-Me exhibits a paramagnetic shift which arises from the long range shielding associated with the anisotropy of the carboxyl carbonyl double bond.

The trans-isomer also provides a clear cut example of coupling ($J = 0.95$ cps.) across four carbon atoms.

L. M. Jackman,
J. W. Lown.

Low Temperature Probe Modification.

The system described is used for examining very unstable compounds where the prime consideration is the rapid transfer of the sample into the pre-cooled apparatus. The sample tubes are spun using the standard Varian turbine and the resolution achieved [see enclosed spectrum of -CH₂- in diethylamine] is adequate for most purposes. The loss in sensitivity, resulting from using the 15mm insert, is not too serious as can be seen from the spectrum [Attenuation ×2 Leakage 100μA]. Temperatures of the order of -150°C have been achieved and kept constant to 1°C for periods of 20 minutes. No modification to the Varian insert is required.

The unsilvered dewar is placed inside a standard Varian 15mm insert and held by a simple support attached to the probe body. The dewar head was made of nylon [low heat capacity] and it was found necessary to have an 'O' ring as shown to prevent its sinking into the B.29 socket on contracting and subsequently causing damage on warming up. The temperature was measured with a thermocouple which passed through the dewar head and was taken as close to the sample as desired for any particular purpose.

To prevent condensation within the insert a cotton wool sleeve was fitted around the dewar above the insert entrance. The low temperatures are reached and maintained by a stream of cold N₂ gas supplied by a liquid N₂ boiler.

J. FEENEY
L.H. SUTCLIFFE

H Resonance at 40 Mc/s of -CH₂- group in diethylamine.

LOW TEMPERATURE PROBE MODIFICATION
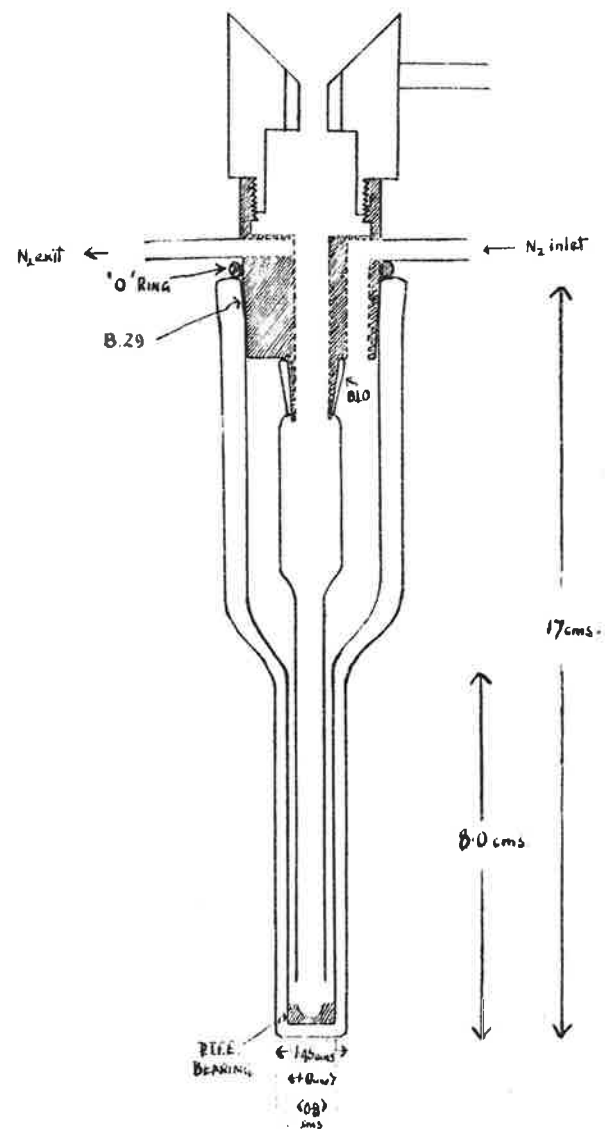
THE SEPARATION OF CLOSELY-SPACED BANDS BY THE 'WIGGLE BEAT' METHOD

- J. Lee -
Department of Chemistry, The Manchester College of Science and
Technology, Manchester, 1.

When, because of resolution limitations, the separation of two
absorption bands in a spin-spin multiplet is too small to permit
direct measurement, it may be possible to apply the 'wiggle beat'
method of C. A. Reilly[1]. Instead of the simple exponential decay
(with characteristic time T_2) for the wiggles following a single
band - assuming a sufficiently rapid field or r.f. sweep and a
linear audio response in the receiver - a more complex pattern
arises in which the envelope equation takes the form

$$V_1(t) = 2V_0 e^{-t/T_2} \cos \pi x t , \qquad ----- (1)$$

where V_0 is the maximum amplitude of the absorption band, t is the
time effectively measured from this maximum and x is the band sep-
aration (in units of time^{-1}). The time interval between adjacent
extrema of $V_1(t)$ is then simply the inverse of x. Reilly states
that it is also possible to derive the band separation from the
time interval between the band maximum and first $V_1(t)$ extremum
but that here a knowledge of the transverse relaxation time is
required; the relationship is not presented.

We have examined several spectra[2] in which the close-band sep-
aration and transverse relaxation time are such that only the first
beat envelope extremum appears in the recording and in such cases
we have had to resort to calculating the splitting from the
T_2-dependent interval (designated t_m). Fortunately, other bands in
the spin-spin multiplet were sufficiently isolated to allow
a reasonable estimate of T_2 by wiggle decay measurement (although
some estimate could be made from band widths even in the absence
of additional bands). t_m is related to x and T_2 by

$$t_m = \left[(1/\pi x) \tan^{-1}(-1/\pi x T_2) \right] \text{ value between } 1/2x \text{ and } 1/x. \quad ---(11)$$

In Fig. 1 t_m is plotted against 1/x for various values of T_2. Certain
facts emerge:

    (1) Even if T_2 is completely unknown, limits may be applied to
        the band separation.
    (2) The maximum value of the separation is twice the minimum.
    (3) The smaller the band separation, the more precisely does
        one need to know the transverse relaxation time.

A typical application of the method is to $CH_2Cl.CF_2Br$, an A_2X_2
case[3][4] in which $J_{HF} \neq J_{HF'}$ and $J_{FF} \gg J_{HH}$, J_{HF}, $J_{HF'}$. With 'max-
imum' audio filtering, both the ^{1}H and ^{19}F spectra appear as a
1:2:1 triplet but if the filtering capacitance is removed from the
audio stage of the receiver (a fifth position may be added to the
Frequency Response switch of the Varian V4300B 40 Mc/s Spectrometer
corresponding to open circuit by moving the stop), the wiggle pattern
after the central band indicates a doublet nature (Fig. 2). From
an estimation of T_2 from the outer bands (separated by 12 sec^{-1} from
the central bands) and a measurement of t_m (the markers in the
lower trace are at 1 second intervals), the doublet splitting
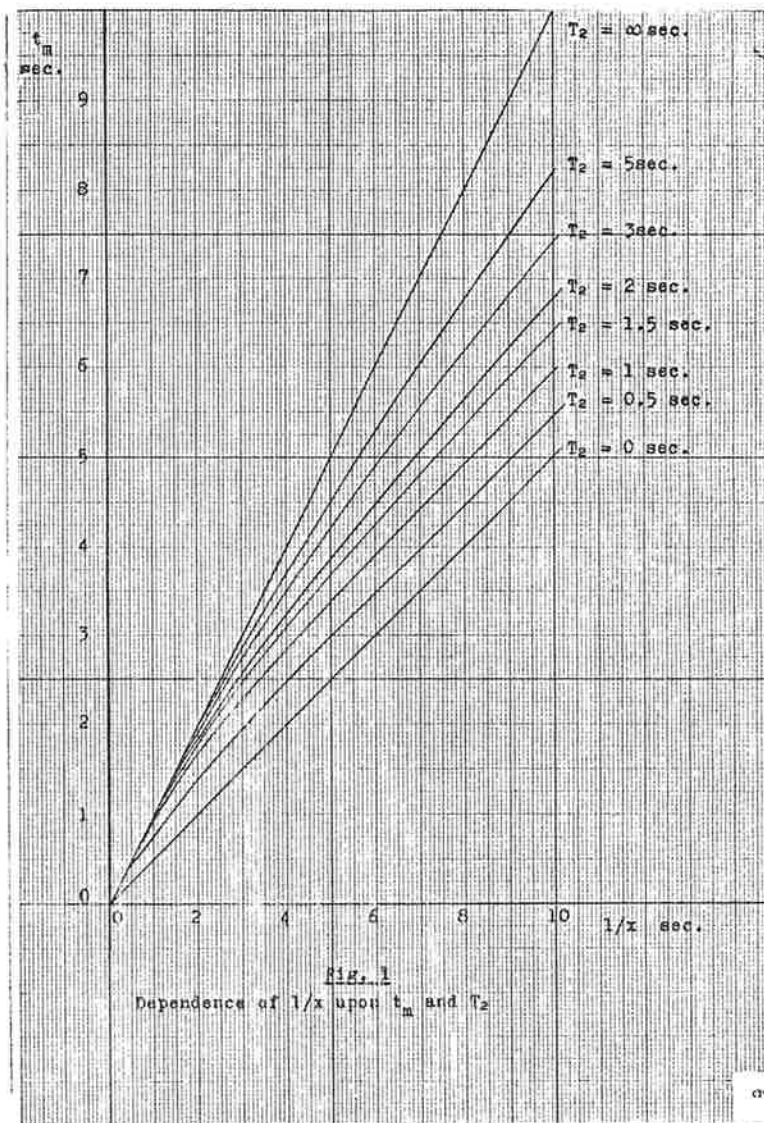(a function of J_{HF}, $J_{HF'}$ and J_{FF}) is estimated as 0.4 sec^{-1}.

Fig. 1

Dependence of 1/x upon t_m and T_2

[1] C. A. Reilly, J. Chem. Phys., 1956, 25, 604
[2] The experimental work was performed in the Department of Inorganic and Physical Chemistry, The University, Liverpool, 7.
[3] McConnell, McLean and Reilly, J. Chem. Phys., 1955, 23, 115
[4] Pople, Schneider and Bernstein, Can. J. Chem., 1957, 35, 1060

Fig. 2 ^{1}H spectrum of $CH_2Cl.CF_2Br$ at 40 Mc/s

2,4,5,6 TETRAFLUORO-PHENYLENEDIAMINE

^{19}F RESONANCE

Provisional measurements and analysis.

Type AB$_2$
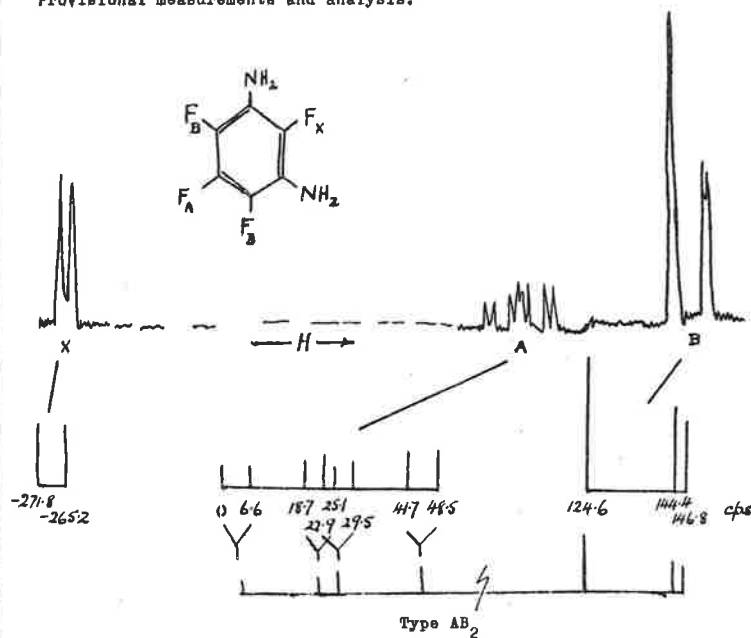
Spectrometer: Mullard SL44 MkI	$\delta_A - \delta_X$	: 9.8 ppm
Frequency : 30.11 Mcps	$\delta_B - \delta_X$	: 13.4 ppm
Solvent : Acetone	J_{AX}	: 6.6 cps
Conc. : 3M	J_{AB}	: 21.3 cps
Temp. : 34°C	J_{BX}	: < 2 cps

L.F.Thomas,
Department of Chemistry,
University of Birmingham.
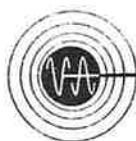
VARIAN associates

611 HANSEN WAY · PALO ALTO, CALIFORNIA · DAVENPORT 6-4000

August 13, 1959

Drs. A. A. Bothner-by and B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Aksel and Barry:

I should like to start this letter out by congratulating you on the work you have been doing in getting out the MELLONMR News Letter. This is really a tremendous service to all NMR spectroscopists and I feel that you cannot be commended highly enough for undertaking it.

I was a little surprised when I opened issue No. 10 and discovered that not only are journal referees now served with a set of requirements for judging the acceptability of NMR papers but are even provided with a "guide" in order to make sure that they do not inject their own opinions. I feel rather reluctant to take issue with this apparently well-meant effort, but feel that I must point out the danger in taking away from referees the prerogative of exercising their own judgment.

I think many of the points which George Tiers has made are well taken, and had these been presented under the heading "suggestions for journal referees" I would have been inclined to let the matter pass without comment. However, to use an analogy, the presentation of a set of requirements for journal referees is rather like a baseball player presenting the umpire with a set of instructions on how to call the balls and strikes as he steps up to the plate.

The guide would be more pertinent if all NMR papers were concerned solely with the presentation of spectral data for catalog purposes. However, one must not lose sight of the fact that the major purpose of many papers is to solve a specific problem, and the presentation of supporting data is in a sense a by-product. Quite often, the problem can be solved without exhaustively obtaining all possible data, although the catalog value of the partial data is reduced or possibly even eliminated. Nevertheless, we cannot insist that every chemist measure all line positions with great precision and report them in a certain form if a single line frequency or a shift in position of some line would have permitted a solution of the problem at hand.

With one or two points I simply cannot agree. I do agree that chemical shifts should be reported in field independent units, but when these are derived quantities rather than directly observed, the frequencies of the multiplet lines from which they are derived should be given. After all, the author may not have performed the calculation correctly. In most NMR spectra,

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VARIAN associates

Drs. A. A. Bothner-by and B. L. Shapiro   -2-   August 13, 1959

there are more lines than not which owe their position to a combination of chemical shift and spin coupling perturbations so that they cannot be described in field independent units. I also do not agree with the statement that we should always omit figures if data can be tabulated. Obviously, it is desirable to avoid figures where possible for space reasons (as every journal editor already suggests) but since no NMR spectrum is ever interpreted with complete objectivity by its proud owner, there are many subtle details which can escape detection if they are conveniently withheld from the reader. If the old saying "one picture is worth a thousand words" is true, I even question whether we save much space by leaving suitably chosen figures out of the journals. In any case, lets leave it up to the referee to decide.

In order not to give the impression that this letter is an entirely negative one, I would like to present some recent findings in our laboratory concerning the NMR spectrum of methyl acetylene. This molecule is an A_3B system of nuclei with a J/δ ratio of 1.33. Analysis of this nearly accidentally degenerate multiplet results in a best fit of experiment and theory for $J = 2.9 \pm 0.1$ cps and $\delta = 2.2 \pm 0.2$ cps (0.037 ppm). We have, however, measured these quantities more accurately from an analysis of the spectra of all three of the molecular species containing one C^{13} nucleus in natural abundance. A table of observed frequencies is included which will be submitted for publication along with a more detailed account of this work.

Signals Observed (underlined)	ν (cps)[a]	J_{HH}(cps)[b]	J_{C13H}(cps)	Average
$C^{13}H_3-C^{12}\equiv C^{12}H$	172.9, 170.0	2.9	131.4	105.75±0.07
	41.5, 38.6	2.9		
$C^{12}H_3-C^{13}\equiv C^{12}H$	99.1, 102.0	2.9	10.6	105.85±0.07
	109.7, 112.6	2.9		
$C^{12}H_3-C^{13}\equiv C^{12}H$	129.9, 131.9, 134.8, 137.6	2.9	50.8	107.90±0.05
	78.0, 81.0, 83.9, 86.9	2.9		
$C^{12}H_3-C^{12}\equiv C^{13}H$	227.3, 230.3, 233.2, 236.1	2.9	247.6	107.86±0.05
	-20.5, -17.5, -14.5, -11.6	3.0		

a) Individual line frequencies were each measured several times and averaged. The standard deviation for these measurements is ±0.1 cps. The reference compound was tetramethyl silane in a capillary tube.
b) Average of consecutive line separations in second column.

The measurements of the table allow us to state that $J = 2.93 \pm 0.05$ cps and $\delta = 2.1 \pm 0.1$ cps (0.035 ppm).

In addition to the frequencies reported in the table, we have found some very weak lines, symmetrically located about the chemical shift positions for the two types of protons, which fall among the weak lines of the A_3B pattern of the isotopically normal molecule, and which are located on the absorption wings of strong lines several cycles away and between one and two thousand times as intense. For this reason we were prevented from observing all of the lines of the multiplets and therefore attach less certainty to the assignments. If our assignments are correct, $J_{C^{13}H}$ for the methyl group in the species $C^{12}H_3-C^{12}\equiv C^{13}H$ is 4.8 cps and $J_{C^{13}H}$ in the species $C^{13}H_3-C^{12}\equiv C^{12}H$ is 4.5 cps for the proton on the carbon atom at the opposite end of the molecule from the C^{13}. It would seem that with this complete set of $J_{C^{13}H}$ coupling constants we ought to be able to see some relationships between them which are related to the electronic structure of the molecule.

Congratulations again on the terrific job you are doing with MELLONMR.

Sincerely yours,

James N. Shoolery

James N. Shoolery
Varian Associates

JNS:mjr

IBM 704 COMPUTATION OF NMR SPECTRA

A program for the IBM 704 computer has been developed which accepts as raw data: NUCLEI, the number of spin 1/2 nuclei (up to 7); W(1) through W(NUCLEI), the chemical shifts (in cps); and A(1,2), A(1,3)...A(NUCLEI-1, NUCLEI), the coupling constants; and produces a tabulation of the spectrum, giving positions and intensities for all lines. The compiled program is available in SAP language. Arrangements for temporary loan of a program deck, which is easily duplicated, can be made.

The machine output is at present on magnetic tape. The tape is transferred to an off-line printer, in order to conserve machine time. If an off-line printer is not available a minor modification of the program will allow direct read-out or the punching of output data cards.

Typical times required for the calculation of one spectrum are

$$
\begin{array}{lll}
3 \text{ nuclei} & \sim 0.001 \text{ hr.} \\
4 \text{ nuclei} & \sim 0.004 \text{ hr.} \\
6 \text{ nuclei} & \sim 0.14 \text{ hr.}
\end{array}
$$

These times do not include the time required to read the program into the machine.
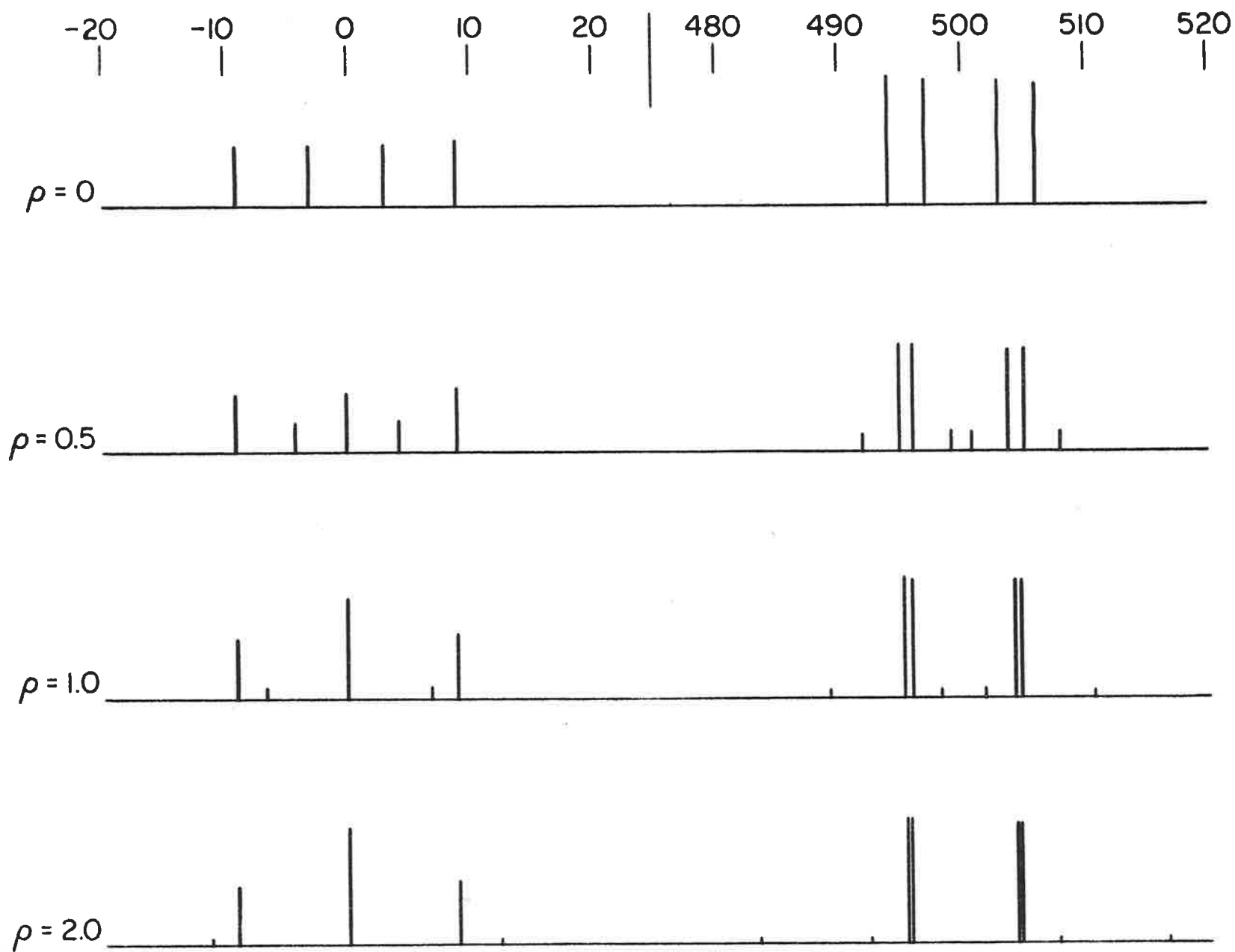
A. A. Bothner-By, C. Naar-Colin, C. P. Saalbach

A note on AXX' where $J_{AX} \neq J_{AX'}$

In the interpretation of spectra of organic compounds, the situation is often encountered that one proton is differently coupled to two other protons which are themselves coupled. In the BSF representation, the case is AX_2 (or AB_2) where $J_{AX} \neq J_{AX'}$ and $J_{XX'} \neq 0$. If the XX' coupling were in fact zero, one would observe for the A's and for the X's a doublet of doublets. It is intuitively attractive, if not readily logically demonstrated, that as the XX' coupling is increased, the X_2 part of the system will behave more and more like a unit, and the pattern will tend toward a 1-2-1 triplet for the A and a 1-1 doublet for the X's. The sensitive parameter will be of the form $\rho = J_{XX'}/(J_{AX} - J_{AX'})$. Some calculations performed on a sample case demonstrate that the change over from one pattern to the other occurs surprisingly fast.

The cases calculated were $J_{AX} = 12$, $J_{AX'} = 6$, $J_{XX'} = 0$, 3, 6, 12 or $\rho = 0$, 0.5, 1.0, 2.0. The chemical shift was taken as 500 cycles. The results are plotted below.

Caution is clearly indicated in drawing conclusions based on an apparent absence of diverse, (e.g. *cis*, *trans*) spin-spin couplings in an observed spectrum.

A. A. Bothner-By
Mellon Institute
Pittsburgh 13, Pa.

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Mellon Institute
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